SILICIDE FORMATION AND SCHOTTKY BARRIER OF RARE-EARTH METALS ON SI

Semi-Annual Technical Report

Reporting Period: January 1, 1982 - June 30, 1982

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Sponsored by: Defense Advanced Research Projects Agency
ARPA Order No. 3011-4276

Contract No. MDA 903-81-C-0348

Effective: June 1, 1981

Expiration: September 30, 1983

Contractor: University of California, San Diego
Office of Contract and Grant Administration
Q-023
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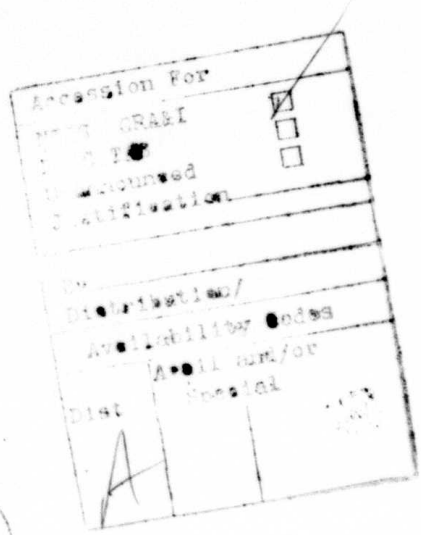


I. INTRODUCTION

During this period, our activities included the following:

(1) Design and construct mechanical masks for Er (and other thin film) depositions.

(2) Completion of the construction of a vacuum annealing furnace. The vacuum chamber is pumped by a turbo-molecular pump and is capable of annealing eight (8) different samples sequentially in one pump-down. The normal operating pressure is $< 2 \times 10^{-7}$ torr and the chamber is relatively free from carbon and oxygen contamination.

(3) Investigation of annealing Er layers deposited on Si in our new vacuum furnace, and the electronic properties of $ErSi_2$ diodes using mechanical masks.

(4) Acceptance of publication by Applied Physics Letters of our paper entitled "Surface Morphology of Erbium Silicides" (see Appendix A).

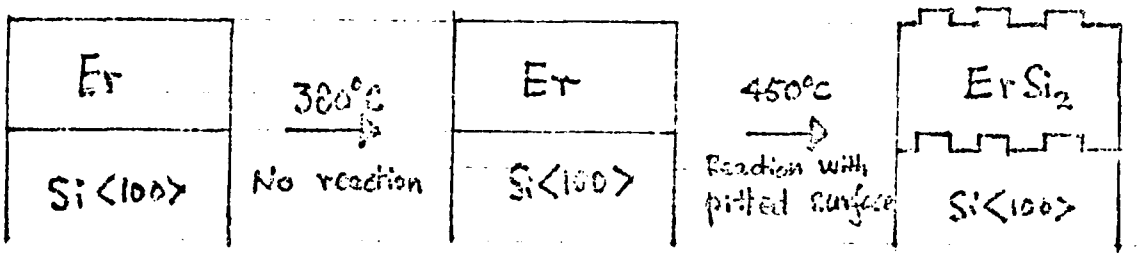
(5) Completion of reviewer paper (with Marc-A. Nicolet) entitled "Formation and Characterization of Transition Metal Silicides", to be published as a chapter in VLSI Electronics: Microstructure Science, Norman Einspruch, Series Editor, Supplement A - Materials and Process Characterization, Graydon Larrabee, Guest Editor, (Academic Press, New York, in press), see Appendix B.

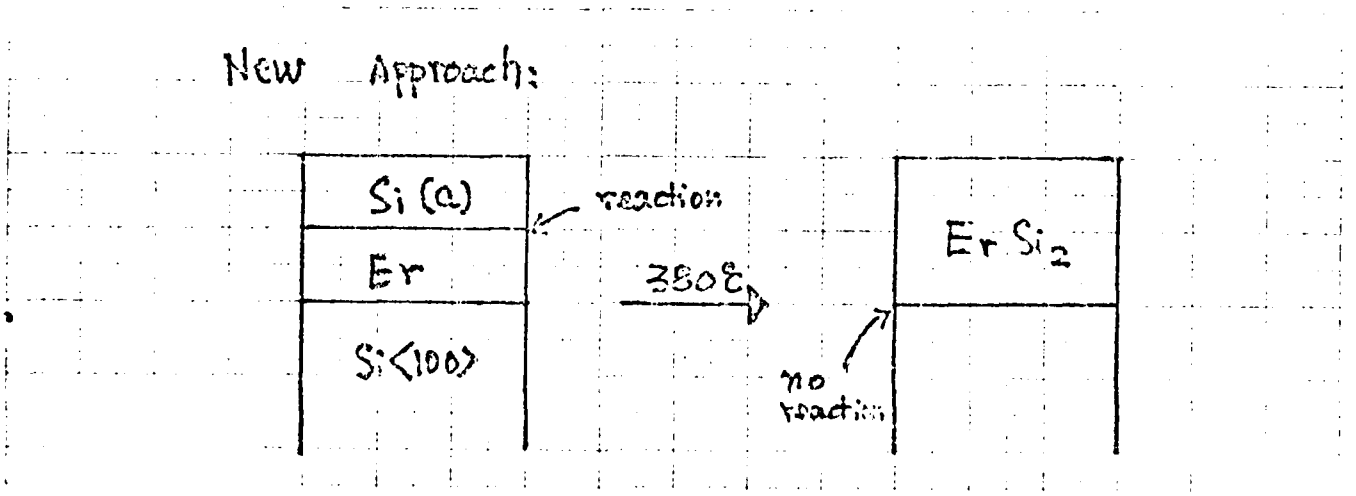
II. SUMMARY OF RECENT RESULTS

(1) We found that mechanical masking is suitable for Er silicide diode fabrication.

(2) Severe oxidation of Er surface during annealing can now be reduced by using the newly constructed vacuum furnace.

(3) Although a typical $ErSi_2$ surface is heavily pitted, we found three ways to reduce or eliminate pitting (see Appendix A paper). Surface pitting has serious effects on the diode performance: (1) a factor of 200 to 1000 higher reverse current (V_R = 10V) and (2) lower barrier heights (the lowering is 0.1 to 0.15 V on p-type Si) are observed. Of the three methods to eliminate surface pitting, the most convenient way is to induce reaction between amorphous (evaporated) Si and Er without any reaction between Er and the Si single crystal substrate. The situation is sketched as follows:





Two factors make this approach amendable to fabricate pit-free $ErSi_2$: (1) Er does not react with single crystal Si below ~ 400°C (critical temperature phenomenon), and (2) Er reacts in a layer by layer manner with amorphous (evaporated) Si at temperatures as low as ~ 300°C. The resulting silicide layer ($Er + 2\ Si(a) \rightarrow ErSi_2$) is pit free. With this approach, it is possible to form a pit-free and stable silicide on p-type Si with a barrier height of ~ 0.75 V or higher. The reverse bias characteristics are much improved compared to those obtained by direct reaction between Er and single-crystal Si substrate.

We also note that Er layers deposited by e-gun evaporation from a Cu hearth always lead to low barrier heights (on p-type Si) and pronounced recombination-generation region in I-V measurements, especially after vacuum annealing. When we switch to thermal evaporation of Er with a tungsten boat, the barrier height increases with vacuum annealing with little or no recombination-generation-region in the I-V curves. We suspect that Er layers deposited by e-gun were contaminated by Cu from the hearth and that Cu diffuses in the Si substrate upon annealing resulting in significant recombination-generation current and low barrier heights.

III. SUMMARY OF APPENDED PAPERS

A. Surface Morphology of Erbium Silicides

The surface of rare-earth silicides is typically dominated by deep penetrating, regularly shaped pits. These pits have been found to have a detrimental effect on the electronic performance of Schottky diodes made from these silicides. This study suggests that contamination at the metal-Si interface is the primary cause of surface pitting. These pits may be reduced or eliminated entirely through (1) the use of Si substrate surfaces prepared under ultra-high vacuum conditions prior to metal deposition or (2) by means of ion implantation techniques.

It is due to these results that we take the approach mentioned in Section II.

B. Formation and Characterization of Transition Metal Silicides

This is a reasonably extensive review, written together with Professor Marc-A. Nicolet at Caltech, on the reaction kinetics under steady state and transient (i.e. laser and electron beam) annealing conditions, oxidation, structural, chemical and electrical properties of transition metal silicides. Although the amount of information accumulated over the past 10-15 years on silicides is immense, there are still numerous questions that require further clarification. It is important to recognize, we believe, that the dominant moving species during silicide formation may be an important issue for the application of silicides to VLSI technology. This is because of the limitation of lateral confinement in small structures and the defects left inside the Si substrate after silicide formation if Si is the moving species. In the case of commonly used refractory silicides (i.e. $MoSi_2$, WSi_2, $TaSi_2$ and $TiSi_2$) in

VLSI applications, Si is found to be the moving species. Cautions as well as novel techniques must be exercised in fabricating these devices.

Due to the length of this review article (over 300 typed pages), the entire paper will not be included in this report. The table of contents and the acknowledgment are included instead.

APPENDIX A

To be published in Applied Physics Letters.

SURFACE MORPHOLOGY OF ERBIUM SILICIDE

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The surface of rare-earth silicides (Er, Tb, etc.), formed by the reaction of thin film metal layers with a silicon substrate, is typically dominated by deep penetrating, regularly shaped pits. These pits may have a detrimental effect on the electronic performance of low Schottky barrier height diodes utilizing such silicides on n-type Si. This study suggests that contamination at the metal-Si or silicide-Si interface is the primary cause of surface pitting. Surface pits may be reduced in density or eliminated entirely through either the use of Si substrate surfaces prepared under ultra high vacuum conditions prior to metal deposition and silicide formation or by means of ion irradiation techniques. Silicide layers formed by these techniques possess an almost planar morphology.

The solid state interactions between rare-earth metals (such as Er, Tb) and single-crystal Si exhibits a "critical temperature" phenomenon[1,2,3]. Below the critical annealing temperature, interactions are very sluggish and often escape detection. Above the critical annealing temperature, interactions are so fast such that reaction kinetics cannot be investigated. The formation of rare-earth metal silicides is characterized by the observation that Si is the dominant moving species during interactions[3]. The surface morphology of the silicide is typically dominated by a heavy pitting. The pitting is often crystallographic in nature exhibiting the symmetry of the underlying Si substrate. These rare-earth silicides form a low Schottky barrier height, ϕ, to n-type Si with $\phi \cong 0.4$ eV[4,5]. The presence of surface non-uniformities, could prove to have a detrimental effect on the electronic performance of Schottky barrier devices. The present study examines the origin of this surface pitting and presents several means by which a smooth planar morphology can be achieved.

Two types of structures were initially investigated in order to determine the role of the crystalline Si substrate in surface pitting. In the first structure, $ErSi_2$ was formed by the reaction of a layer of Er deposited onto a single crystal Si substrate while in the second structure the silicice was formed by the reaction of Er with an amorphous Si layer. Specifically, substrates of <100> Si used in both structures were first cleaned by organic solvents and then etched in a dilute HF solution, prior to loading into an ion-pumped vacuum chamber. The base pressure of the chamber was ~5 x 10^{-8} torr and the pressure during E-gun evaporation (~10Å/sec) was ~1 x 10^{-7} torr. In the first substrate the deposited layer of Er (~1700Å) was reacted with the Si substrate by annealing at 450°C in vacuum (~10^{-6} torr) to form $ErSi_2$. The resulting surface morphology can be seen in the cross-sectional micrograph of Figure 1. The pits are generally a few μm in size and penetrate deep into

the Si substrate with a depth generally 2 to 3 times the total silicide thickness. The pits possess a square or rectangular shape on <100> Si, thus suggesting that the pits are related to the crystalline nature and orientation of the Si substrate.

The second structure was formed by the sequential deposition of first Si (~5000Å) then Er (~1700Å) onto a <100> Si substrate without breaking vacuum between depositions, Tsaur and Hung[6] have shown that the metal/amorphous Si interface in samples prepared by sequential deposition without breaking vacuum is relatively free of contamination compared to that of metal/crystalline Si samples cleaned chemically; and the thickness of silicide now increases as $(\text{annealing time})^{\frac{1}{2}}$. The amorphous Si thickness used here was more than enough to react completely with the Er layer to form $ErSi_2$. These silicide formation characteristics are in marked contrast to those observed on Er/<100> Si samples, After annealing at 450°C, the silicide surface appeared undulated (typical of most silicide) but free of pits. This can be seen in Figure 2.

The absence of deep surface pitting in the Er/Si(a) structure may be due to either unique interfacial reactions present in the Er/Si(a) system because of the amorphous nature of the substrate or the relative cleanliness of the Er/Si(a) interface.

Two experiments were performed to further ascertain the origins of the silicide surface pitting. The first experiment consisted of preparing Er/<100> Si samples in ultra-high vacuum (UHV) to obtain a clean Er/crystalline Si interface. A thin thermal oxide (~2000Å) was first grown on the <100> Si substrate, the oxide layer was then etched off with a 10% $HF-H_2O$ solution, followed by immediate loading into an ion pumped vacuum chamber. Once a vacuum of $\sim 5 \times 10^{-10}$ torr was obtained, the Si substrate was backside heated to 500-600°C. This heating resulted in the desorbtion of mainly Flourine atoms (originating from HF used on the Si surface) from the substrate surface as determined by a residual

gas analyzer. After cooling to room temperature, the substrate Er (~1300Å) was deposited onto the Si surface at a rate of 10-20Å/sec. The chamber pressure was 10^{-9} torr during deposition. We believe the Er/<100> Si interface thus prepared is much cleaner than that for the sample shown in Figure 1, although no chemical analysis was done on the samples[7,8]. After silicide formation, the surface possessed a low density of very shallow pits (see Figure 3). This experimental result indicates that relatively clean Er/crystalline Si interface leads to little or no surface pitting.

Ion mixing technique was used to modify the silicide surface morphology in a second experiment. It has been shown that interfacial contaminants such as thin oxide layers interlaced between a metal layer and Si substrate can be "broken-up" and dispersed, thus allowing silicide formation to proceed as if the oxide layer was absent[9]. In our case, Si ions were used to irradiate a sample of Er (1700Å)/<100> Si. The irradiation was done at 300 keV with a dose of 5×10^{15} Si^+/cm^2 at room temperature. Under these conditions, the Si substrate near the Er/Si interface would be damaged by irradiation, however, the silicide reaction after annealing would consume more than the implantation damaged region in the Si substrate (the damaged thickness in Si is estimated to be ~1300Å). The silicide layer would then contact relatively damage-free Si after the silicide formation. The surface of such a sample (after implantation and annealing) is again relatively free of pits as illustrated in Figure 4. This experiment again points to the role of surface impurities or contamination in the development of a rough and pitted morphology.

Differences in the physical structures of the silicide formed under the varying experimental conditions were also investigated in this study. X-ray diffraction experiments (Read Camera) showed that $ErSi_2$ layers formed by various processing steps have hexagonal structure, as reported before[1,3] (although the composition was found to be $ErSi_{\sim 1.7}$ by MeV He^+ backscattering techniques)[3].

However, strong texture [(100)$ErSi_2$//(100)Si] was observed for $ErSi_2$ formed on clean <100> Si substrate (sample shown in Figure 3). The texture was so strong that modest channeling effect could be observed by the MeV He^+ beam aligned with the <100> direction of Si. Clean Si surface, therefore, not only promotes pit free silicide formation but also provides a certain degree of epitaxial alignment of the silicide. Silicide layers formed on contamined <100> Si (Figure 1), amorphous Si (Figures 2) and on <100> Si with ion irradiation (Figure 4) were randomly oriented.

All these experimental results are consistent with the idea that interfacial contamination is the cause of surface pits in the silicide layer. We recognize that no chemical analysis (SIMS or Auger) was performed to determine interfacial cleanliness, however, we believe that the experimental evidence is strong enough to draw such a conclusion. We speculate that silicide nucleates initially through "weak" spots at the contaminated interface. Once silicide formation is initiated, reaction kinetics are so rapid that columns of silicide are formed. Silicon atoms from the substrate migrate through the silicide columns and then spread laterally to react with the remaining Er. The silicide between the columns are formed by a lateral growth of the columns and not by a spatially uniform reaction between the remaining Er layer and the Si susbstrate underneath. In such a manner, the initially formed columns are observed as pits. This concept is consistent with the observation that Si is the moving species during silicide formation. On clean surfaces (either by high-vacuum processing or by ion beam dispersion of interfacial contamination), silicide formation proceeds in a uniform manner across the entire sample surface, resulting in a silicide layer which is relatively flat and free of pits . Work is currently underway to determine the effects of varying surface morphology on the electronic performance of silicide Schottky barrier devices.

Acknowledgements

The authors are indebted to Rouel Fernandez for technical assistance. This work is supported by DARPA (MAA 903-81-C-0348, S. Roosild) at University of California, San Diego. The implantation part of this study at Caltech was financially supported by the U. S. Department of Energy through an agreement with the National Aeronautics and Space Administration and monitored by the Jet Propulsion Laboratory, California Institute of Technology, (D. Bickler). We would like to acknowledge Dr. Martti Mäenpää for his participation in the initial stage of this work.

References

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1. J. E. E. Baglin, F. M. d'Heurle and C. S. Petersson, Appl. Phys. Lett. 36, 594 (1980).
2. R. D. Thompson, B. Y. Tsaur and K. N. Tu, Appl. Phys. Lett. 38, 535 (1981).
3. J. E. E. Baglin, F. M. d'Heurle and C. S. Petersson, J. Appl. Phys. 52, 2841 (1981).
4. K. N. Tu, R. D. Thompson and B. Y. Tsaur, Appl. Phys. Lett. 38, 626 (1981).
5. H. Norde, J. de Sousa Pires, F. d'Heurle, F. Pesavento, S. Petersson and P. A. Tove, Appl. Phys. Lett. 38, 865 (1981).
6. B. Y. Tsaur and L. S. Hung, Appl. Phys. Lett. 37, 922 (1980).
7. L. S. Hung, S. S. Lau, M. von Allmen, J. W. Mayer, B. M. Ullrich, J. E. Baker, P. Williams and W. F. Tseng, Appl. Phys. Lett. 37, 909 (1980).
8. S. I. Raider, R. Flitsch and M. J. Palmer, J. Electrochem. Soc. 122, 413 (1975).
9. L. S. Wielunski, C. D. Lien, B. X. Liu and M.-A. Nicolet, J. Vac. Sci. Technol., to be published (1982).

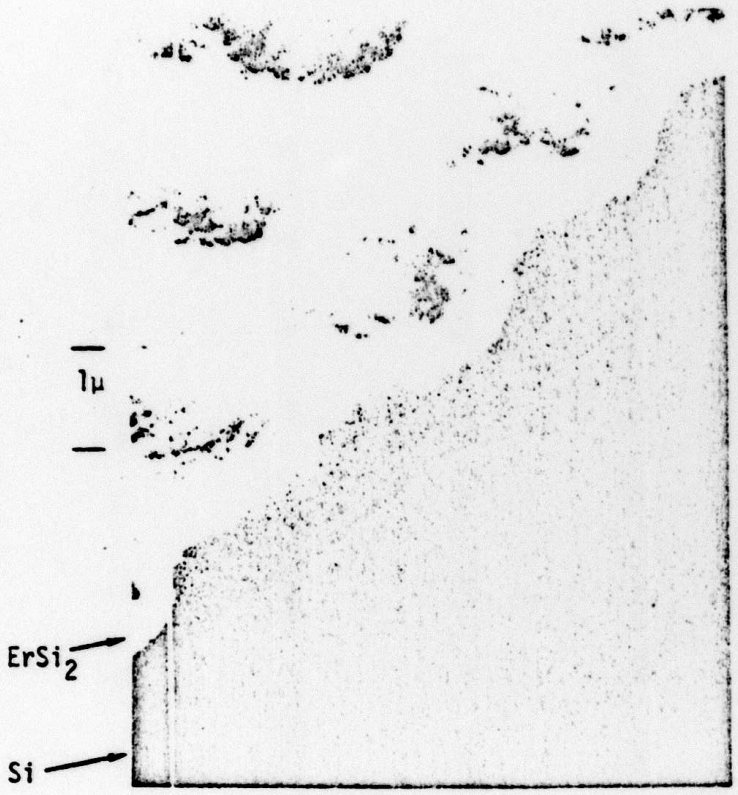
Figure Captions

Figure 1 Surface morphology of $ErSi_2$ on <100> Si, formed by vacuum anncaling (450°C, 30 min) a sample of Er (~1700Å)/<100> Si. (A) scanning electron micrograph of an oblique view, (B) optical micrograph of a top view taken with Normaski interference.

Figure 2 Surface morphology of $ErSi_2$ on amorphous Si, formed by vacuum annealing (450°C, 30 min) a sample of Er (~1700Å)/Si(a,~5000Å)/ <100> Si. (A) scanning electron micrograph of an oblique view, (B) optical micrograph of a top view taken with Normaski interference.

Figure 3 Surface morphology of $ErSi_2$ on <100> Si, formed by vacuum annealing (450°C, 30 min). A clean substrate surface was prepared in situ under a vacuum of ~5 x 10^{-10} torr. (A) scanning electron micrograph of an oblique view, (B) optical micrograph of a top view taken with Normaski interference.

Figure 4 Surface morphology of $ErSi_2$ on <100> Si. This sample [Er(~1700Å)/ <100>Si)] has been implanted with Si ions and then vacuum annealed to form $ErSi_2$. (A) scanning electrom micrograph of an oblique view, (B) optical micrograph of a top view taken with Normaski interference.



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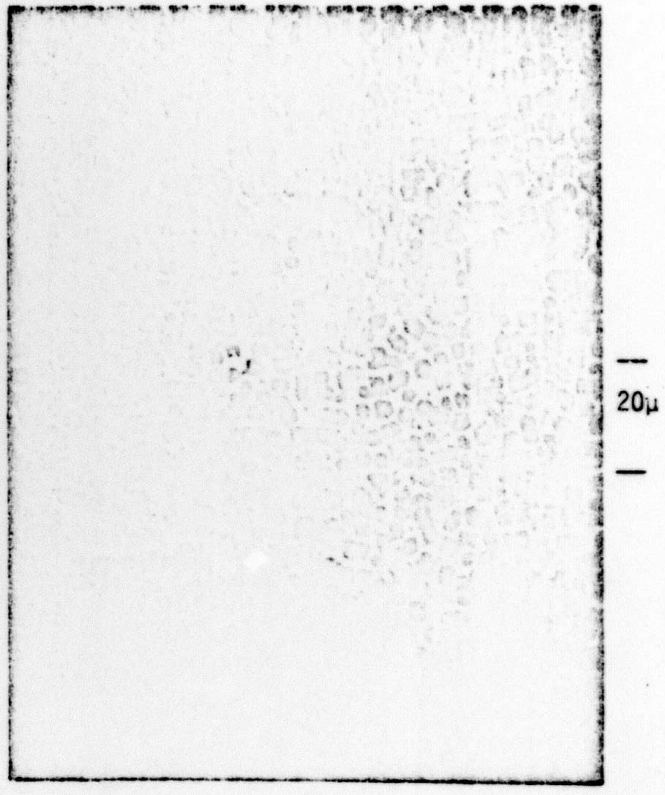

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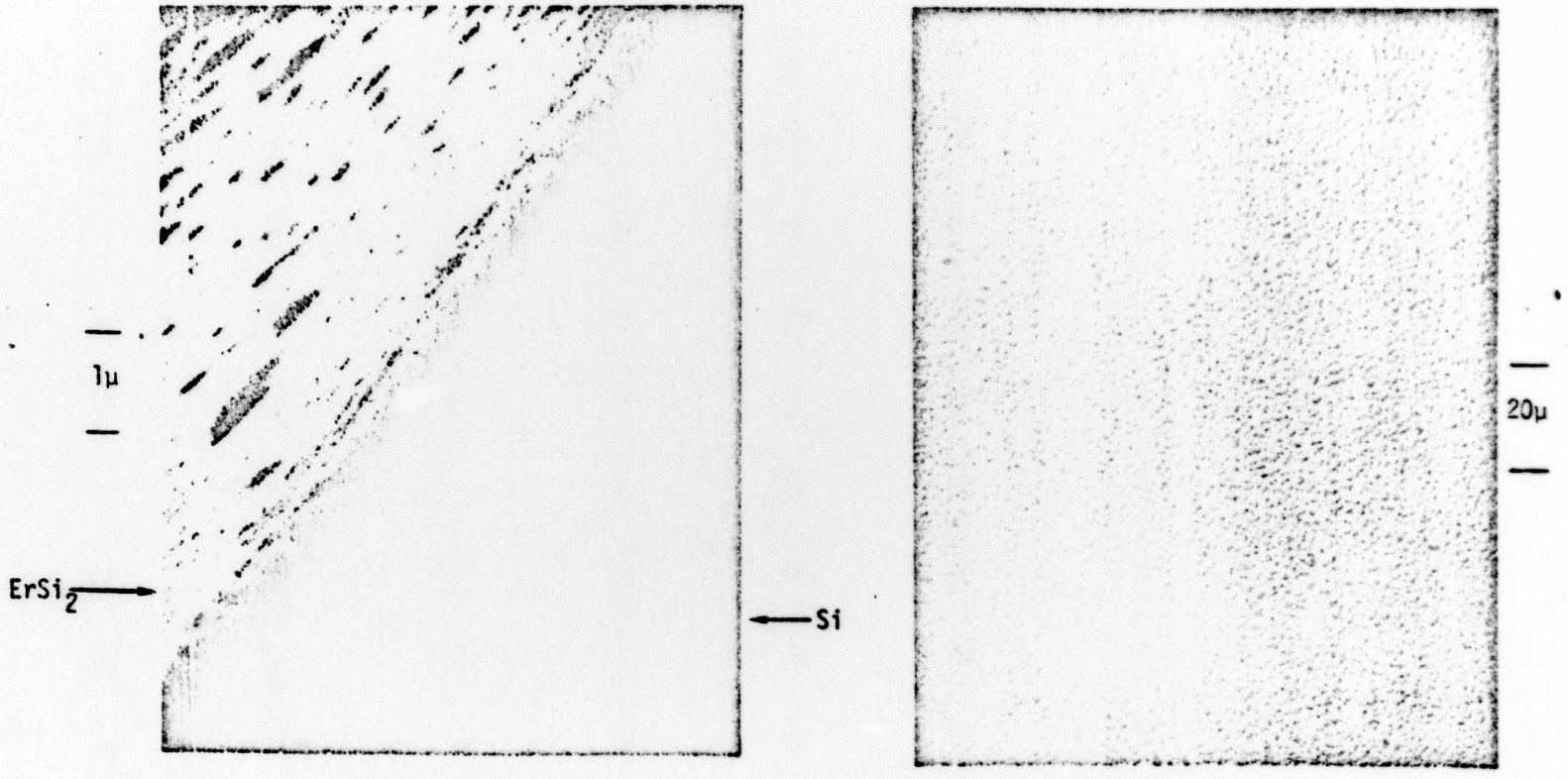

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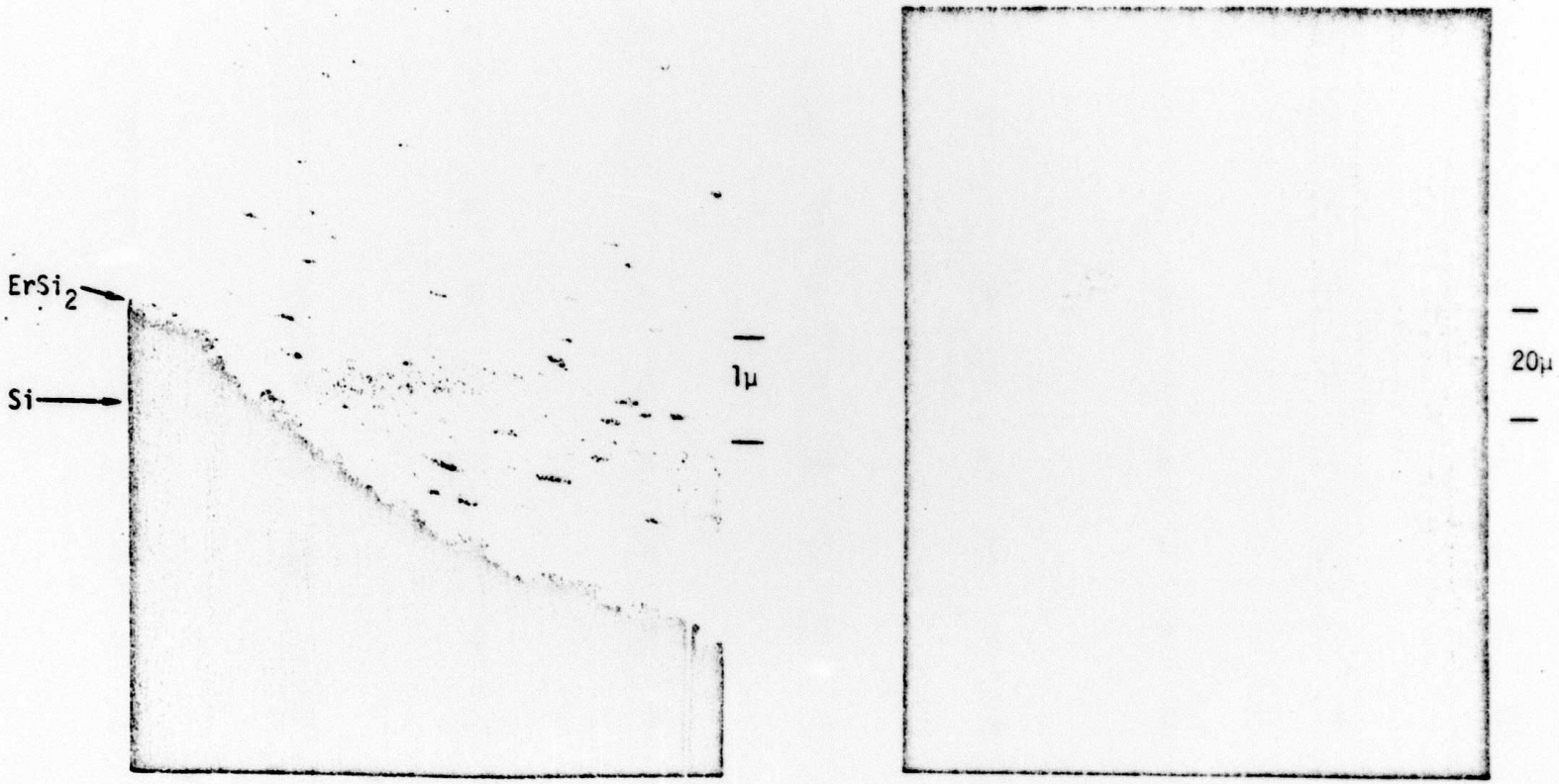

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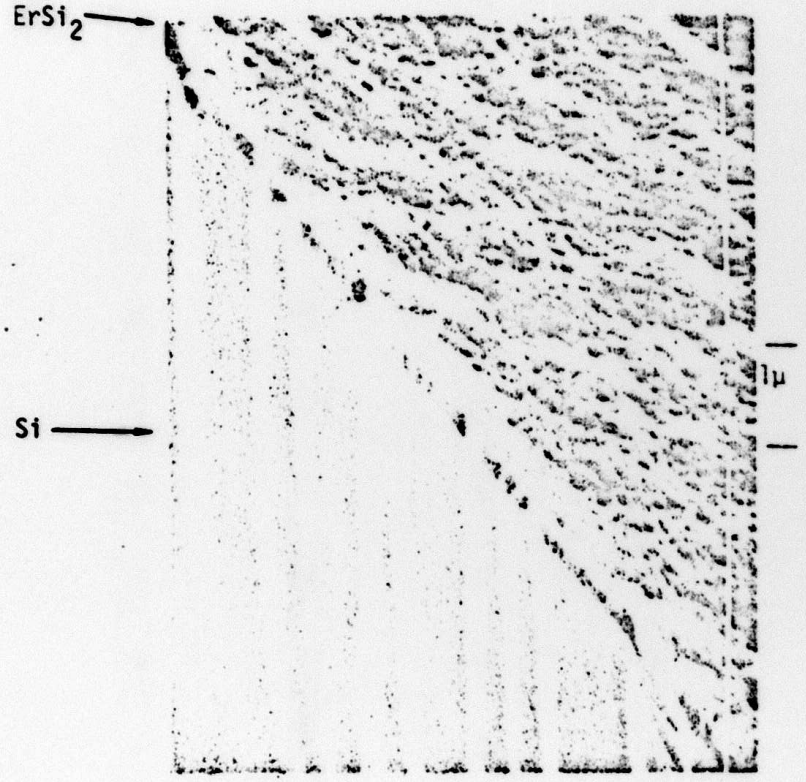

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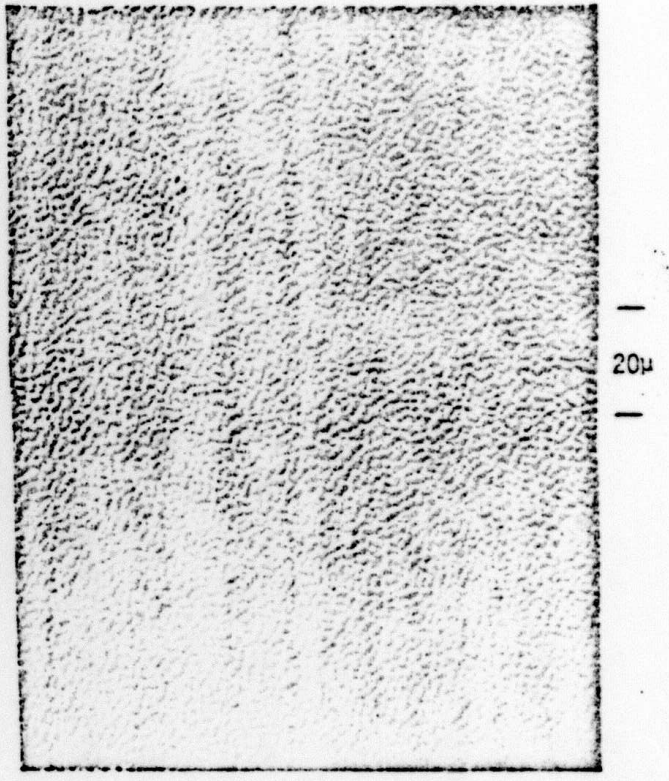

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APPENDIX B

To be published as a chapter in VLSI ELECTRONICS: MICROSTRUCTURE SCIENCE, Norman Einspruch, Series Editor, SUPPLEMENT A - MATERIALS AND PROCESS CHARACTERIZATION, Graydon Larrabee, GUEST Editor, (Academic Press, New York, in press).

FORMATION AND CHARACTERIZATION OF TRANSITION METAL SILICIDES

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V. ACKNOWLEDGMENT

We are endebted to P.E. Duwez (Caltech), W. G. Moffatt (General Electric Co., Schenectady), G. Ottaviani (University of Modena), and E. Wachtel (Max-Planck-Institut, Stuttgart) for assistance in securing the most recent data on the phase diagrams of Ni and Pd. We benefitted of the participation of M. Bartur (Caltech) in compiling the information listed in Tables XVII and XVIII.

F. d'Heurle, P. S. Ho and K. N. Tu (IBM, Yorktown Heights) as well as J. M. Poate and A. K. Sinha (Bell Telephone Labs, Murray Hill) gave us very helpful information and useful comments. We thank them all for their interest and assistance. Particular recognition is due to S. J. Kim (Caltech) who carried the heavy burden of compiling almost singlehandedly the content of the tables in the Appendix from the open literature. The work was partially supported by the U.S. Department of Energy and monitored by Sandia Laboratories, Albuquerque, New Mexico (L. Beavis and M. B. Chamberlain) at the California Institute of Technology, Pasadena, California, and by the Defence Advanced Research Project Agency (S. Roosild), at the University of California at San Diego, La Jolla, California.